Supplementary Information

Determination of Ag⁺ ion by a graphene oxide based dual-output

nanosensor with high selectivity

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Experimental section

Reagents and apparatus

All reagents used were analytical grade. 1, 8-diaminonaphthalene (DAN) was purchased from Sigma. All other reagents were obtained from Shanghai Reagents Company. The deionized water collected from the Millipore purification system was used to prepare these cationic solutions. Atomic force microscope (AFM) image of the GAP was observed using a SPI3800N microscope operating in the contact mode. X-ray photoelectron spectroscopy (XPS) was performed on ESCALB MK-II spectrometer. Fourier transform infrared spectra (FTIR) were recorded on a PE Spectrum One spectrometer with KBr pellets. UV–vis spectra were measured on Perkin Elmer Lambda 35 Spectrometer. Raman spectra were recorded with a Renishaw 2000 equipped by an Ar+ ion laser giving the excitation line of 514.5 nm and an air-cooling charge-coupled device as the detector. X-ray diffraction (XRD) measurements were carried out on a Rigaku D/max 2550V instrument with Cu K α radiation (λ = 1.5406 Å). Fluorescence emission spectra were obtained using AB-series2 luminescence spectrometer.

Preparation of GAP compound

GO was prepared from graphite powder according to the Hummer's method,¹ through the acid-oxidation exfoliation, followed by filtration and vacuum drying. Compound GAP was synthesized according to method that our group reported previously.² The resultant GO (16 mg) was dissolved in 20 mL distilled water under ultrasonication for 1h. 20 μ L N-hydroxysuccinimide (NHS, 1.0 mM) and 20 μ L of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimde (EDC, 1.0 mM) solutions were added to the GO dispersion subsequentlly. After10 min, 10 mL ethanol solution of DAN solution (2 mg/mL) was added. The resulting mixture solution was heated up to 50°C for 2 h, followed by magnetic stirring for 12 h at room temperature. Upon filtration, the GAP was separated and washed by ethanol for subsequent characterization.

Selectivity of Ag⁺ induced fluorescence in the presence of other metal ions.

The selectivity of GAP for Ag⁺ against a background of various alkali, alkaline earth, and transition metal ions was investigated by using fluorescence spectroscopy. Aqueous metal ion solutions of Ag(I), Na(I), K(I), Ca(II), Mg(II), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Fe(III), Al(III), and Cd(II) (perchlorate or nitrate salts) were freshly prepared before use.



Fig. S1. XPS spectra of the GO and GAP. (a) XPS survey spectra of the GO and GAP; (b) C1s peak of GO; (c) C1s peak of GAP;(d) N1s peak of GAP.



Fig. S2. Fluorescence spectra of DAN (black line) and DAN+Ag(I) (red line). The concentrations of DAN and Ag(I) are 2 mg/L and 10 mg/L, respectively.



Fig. S3. Fluorescence spectrum of GO and DAN mixture (excitation at 293 nm). The concentrations are 2mg/L.



Fig. S4. Life time of GAP and GAP+Ag(I) in solutions. The concentrations of GAP and Ag(I) are 2 mg/L and 5mg/L, respectively.

Element	GO		GAP	
	Binding	Relative	Binding	Relative
	Energy	Atomic	Energy	Atomic
	(eV)	Percentage	(eV)	Percentage
C1s (C-C)	285.0		284.63	
C1s (C-O)	286.4		286.63	
C1s (C=O)	287.5	65.21%	287.13	82.77%
C1s (C(O)O)	289.1		not found	
C1s (C-N)	not found		285.53	
N1s (N-C)	not found	0%	399.42	7.96%
N1s (N-C=O)	not found		400.92	
Ols	532.4	34.79%	530.13	9.27%

Table S1. XPS signals and the respective relative atomic percentages of GO and GAP.

Reference

1 W. S. Jr. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, 80, 1339. 2 R. Cheng, Y. Liu, S. Ou, Y. Pan, S. Zhang, H. Chen, L. Dai and J. Qu, *Anal. Chem.*, 2012, 84, 5641.